

after line 17 insert --The layer according to the invention is, however, produced in the absence of any oxidant and consequently free of hexavalent chromium. This can in particular be seen from the fact that the layer according to the invention is not yellow.

Even where the yellow coloration and the enhanced corrosion protection should be brought about by nothing but Ce(IV), the layer according to the invention affords the desired corrosion protection even without this very costly and rare addition.--;

line 26 change "US 4,359,348" into  
--US 43 59 348--;

line 29 change ", thus, is contained in and does not exceed the disclosure of" into --thus does not exceed--; and

after line 30 delete the following "EP 00 34 040 A1 describes a multiplicity of layers, the color of most of them(produced under the standard conditions set forth by Barnes/Ward) although not being specified, is referred to as clear. Examples 16 and 17 of the patent describe a greenish borate-containing layer described as cloudy-dull to non-transparent, and Example 14 describes a layer affording a corrosion protection of only 4 hours."

Page 6, before line 1 delete "SUMMARY OF THE INVENTION";

line 1 change "The" into --It is therefore an object of the--; still line 1 change "thus furnishes" into --to furnish--;

after line 3 delete the following "The layer according to the invention is produced in the absence of any oxidant and is consequently free of hexavalent chromium. This may in particular be seen from the fact that the layer according to the invention is not yellow. Even where the yellow coloration and the enhanced corrosion protection is brought about by nothing but Ce(IV), the layer according to the invention affords the desired degree of corrosion protection, even without this very costly and rare addition.";

after line 15 insert the following  
--EP 00 34 040 A1 does describe a multiplicity of layers, of the larger group of which (produced under the standard conditions set forth by Barnes/Ward) the color is not specified, however referred to as clear. Two Examples, namely Nos. 16 and 17, describe a greenish borate-containing layer described as cloudy-dull to non-transparent.

Example 14 describes a layer affording a corrosion protection of only 4 hours.

The subclaims represent preferred embodiments of the present invention.

Concerning the features of claim 2, the following should be noted:--;

line 26 after "In" delete "one preferred embodiment, upon"; and

line 29 after "content" insert --in %--.

Page 7, line 7 change "drawings" into --drawing, wherein:--;

after line 7 delete "BRIEF DESCRIPTION OF THE DRAWINGS";

lines 7, 8, 10, 13, 15 and 20 change "Figure" into --Fig.--;

lines 9, 12, 14, 15 and 19 change "." into --;--;

lines 16 and 21 change "Figures" into --Figs.--;

after line 19 insert --Fig. 37 is a table containing the evaluation of the depth profile analyses of Figs. 5 to 36.--;

after line 21 insert the following

--Example 1

The following experiment was carried out:

Small steel parts were bright-zinc coated electrolytically (approx. 15  $\mu$ m) and, following galvanization, singly immersed in a boiling (approx. 100°C), aqueous solution containing:--.

Page 8, line 1 insert the following:

-- 100 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt)  
100 g/l  $\text{NaNO}_3$   
15.75 g/l NaF  
26.5 g/l citric acid · 1 aq

which had previously been adjusted to a pH value of 2.5 with sodium hydroxide solution. The immersion time was 30 s. The parts were then rinsed with water and dried in air flow. On the parts a greenish, strongly iridescent layer had formed which later on turned out to be comprised of zinc/chromium oxide. In the corrosion test in the salt spray cabinet according to DIN 50021 SS it was surprisingly found that the chromate layer formed presented a spectacular corrosion protection until the appearance of first corrosion products of 1000 h according to DIN 50961 Chapter 10, in particular Chapter 10.2.1.2.

The novel greenish chromate layer had a layer thickness of approx. 800 nm and was produced by a process not involving any chromium(VI) and could be proven to be chromium(VI)-free.

The production method according to Example 1 for the novel, greenish chromium(VI)-free chromation is not very economical for conventional plants due to the relatively high temperature of the process solution. Further theoretical reflections concerning chromium(VI)-free chromate coating and further trials finally resulted in economical production conditions.

#### **Theoretical Reflections Concerning Chromium(VI)-Free Chromation--;**

after line 23 delete "DESCRIPTION OF THE PREFERRED EMBODIMENTS"; and

line 24 before "Chromate" delete "The".

Page 11, line 1 before "shows" insert --Fig. 38 (originally

Illustration 1)--; and

line 1 delete "The following Table 1 provides an evaluation of a depth profile analysis of Figures 5 to 36.

Table 1: Computer Simulation of Kinetic Model of Chromate Coating of Zn for Various Rate Constants

	Methods								Sample No.
	Ellipsometry nm	SEM nm	Glow-discharge nm (Cr > 1%)	Spectrometer with Cr (%)	Chromium Index	nm (Cr> Zn)	nm (Cr> 30%)		
1. Prior Art (Chromititation)									
Yellow Cr(III) + CR(VI)	-	300	440	11	48	17	25	9	
Blue CR(III)	98	60	60	8	5	0	0	8	
2. Invention (Chromititation)									
60°C Cr(III)	432	300	344	7	23	2	15	1,2,3,4,5	
100°C Cr(III)	595	-	358	10	38	22	28		
60°C on Zn/Fe CR(III)	-	-	282	6	16	0	16	7	
100°C two-fold [Cr(III)]	953	-	-	-	-	-	-		

".

Page 13, line 7 after "2 and 3" delete "below"; and  
after line 7 insert the following

--

Example 2

Electrolytically bright-zinc coated (15  $\mu$ m) steel parts were immersed in an aqueous chromate coating solution containing:

50 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt)  
100 g/l  $\text{NaNO}_3$   
31,2 g/l malonic acid

the pH of which had previously been adjusted to 2.0 with sodium hydroxide solution. The immersion time was 60 s. Following rinsing and drying there resulted in the salt spray cabinet according to DIN 50021 SS a corrosion protection of 250 h until first attack according to DIN 50961.

Malonic acid is a ligand enabling more rapid ligand replacement kinetics at the chromium(III) than the fluoride of Example 1. Good corrosion protection by far exceeding the minimum requirement of DIN 50961 for Method Group C (yellow chromation) may thus already be achieved at 60°C.

#### Example 3

Electrolytically bright-zinc coated (15  $\mu\text{m}$ ) steel parts were immersed in an aqueous chromate coating solution consisting of:

50 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt)  
3 g/l  $\text{Co}(\text{NO}_3)_2$   
100 g/l  $\text{NaNO}_3$   
31,2 g/l malonic acid

previously adjusted to pH 2.0 with sodium hydroxide solution. Immersion time was 60 s. Following rinsing and drying there resulted in the salt spray cabinet according to DIN 50021 SS a corrosion protection of 350 h until first attack according to DIN 50961.

Cobalt is an element which was capable, in accordance with the model concept, of catalyzing ligand replacement and moreover

reducing reverse reaction II owing to insertion of kinetically stable oxides into the chromate layer, so that the chromate layer altogether should become thicker. In this point, as well, the model concept established for the present invention is verified under practical conditions. Corrosion protection could once more clearly be enhanced in comparison with Example 3 by nothing but the addition of cobalt into the chromate coating solution.

Novel greenish chromate layers on zinc were produced in analogy with Example 2 at 40, 60, 80 and 100°C. The layer thicknesses of the respective chromate layers were determined by RBS (= Rutherford-Backscattering) testing. In the Table the corresponding corrosion protection values in hours of salt spray cabinet according to DIN 50021 SS until first attack according to DIN 50961 Chapter 10 are additionally listed.

J/°C	thickness / nm	Corr. Prot. / h
40	100	50-60
60	260	220-270
80	400	350 450
100	800	800-1200

Depending on the complex ligands used, which is malonate in Examples 2 and 3, it is partly possible to achieve even considerably higher layer thicknesses and corrosion protection values. By complex ligands containing as the complexing functional group nitrogen, phosphorus or sulfur, ( $-NR_2$ ,  $-PR_2$  wherein R independently is an organic, in particular aliphatic radical and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H,), it is possible to even produce the indicated layer properties within limits at room temperatures.

#### Example 4

Steel parts electrolytically coated with a zinc/iron alloy (0.4-0.6% iron) were immersed at 60°C in the following aqueous chromate coating solution:

50g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$   
100g/l  $\text{NaNO}_3$   
31.2 g/l malonic acid

The solution was beforehand adjusted to pH 2.0 with NaOH. Immersion time was 60s. Following rinsing and drying a transparent, greenish, slightly grey, strongly iridescent layer was visible on the zinc/iron. In the salt spray cabinet in accordance with the above specified DIN and ASTM standards there resulted a corrosion protection of 360 h until first attack according to DIN 50961.

#### Example 5

Steel parts electrolytically coated with a zinc/nickel alloy (8-13% nickel) were immersed at 60°C into the following aqueous chromate coating solution:

50g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$   
100g/l  $\text{NaNO}_3$   
31.2 g/l malonic acid

The solution was beforehand adjusted to pH 2.0 with NaOH. Immersion time was 60s. Following rinsing and drying a transparent, greenish, dark-grey, strongly iridescent layer was visible on the zinc/nickel. In the salt spray cabinet in accordance with the above specified DIN and ASTM standards there resulted a corrosion protection of 504 h until first attack according to DIN 50961.--.

chromium(III) complex selected from the group consisting of chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and further chelate ligands such as acetylacetone, urea, urea derivatives, and further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur ( $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H); phosphinates and phosphinate derivatives; as well as suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and  $H_2O$  and/or the method is performed repeatedly on the surface to be passivated." into --the enumeration according to claims 9 and 11--; and

line 21 change "The present invention makes it possible for the first time" into --By the present invention it is for the first time made possible--.

Page 17, line 1 change "Yellowish" into --Moreover yellowish--;

line 4 change "there are no known" to --the applicant - one of the leading enterprises in the field of surface technology - is not aware of any--; and

lines 8, 10, 13 and 20 change "Figure" into --Fig.--.

Page 18, lines 1, 6, 9 and 17 change "Figure" into --Fig.--;

line 12 change "The" into --Based on the--;  
line 12 change "shows" into --it therefore results--; still line 13 after "like" delete "those obtained";  
line 14 after "however" delete ","; and  
lines 20 and 24 change "Figures" into --Figs.--.



Page 19, line 3 change "A" into --It is worth mentioning that a--; still line 3 change "in accordance with" into --of--;

lines 5-6 change ". In contrast, even a" into --, whereas even the--;

line 19 after "transparent" delete "of the above referenced patent";

line 22 before "Example 15" insert --In--, and after "040" delete "describes"; still line 22 after "layer" insert --is described--.

line 27 change "present only" into --only present--; and still line 27 do not start new paragraph with "the layer according to".

Page 20, line 1 after "17" delete "of EPO 00 34 040"; and

lines 21, 27 and 30 change "Figure" into --Fig.--.

Page 21, lines 1 and 3 change "of EP 00 34 040" into -- - prior art - --;

line 10 change "Figure" into --Fig.--;

line 30 change "Figures" into --Figs.--.

Page 22, line 1 change "Table 2 below" into --The following Table--;

lines 1-2 change "the calibration is valid." into --calibration is valid:--;

before the table, delete "Table 2:  
Concentration Range for Calibration";

in the line between tables change "results in the following Table 3." into --following Table:--;

before the second table, delete "Table 3:  
Samples' Information".

Page 23, after the table, line 1 change "Figure" into --Fig.--; and after line 3 delete  
**"EXAMPLES."**

### **Example 1: Coating of Zinc Coated and Galvanized Steel Pieces**

Small steel pieces were bright-zinc coated electrolytically (approx. 15  $\mu\text{m}$ ) and, following galvanization, singly immersed for 30 seconds in a boiling (approx. 100°C) aqueous solution containing the following components:

- 100 g/l  $\text{CrCl}_3 \cdot \text{H}_2\text{O}$  (trivalent chromium salt),
- 100 g/l  $\text{NaNO}_3$ ,
- 15.75 g/l  $\text{NaF}$ , and
- 26.5 g/l citric acid  $\cdot$  1 aq.

The solution had previously been adjusted to pH 2.5 with sodium hydroxide solution. The parts were then rinsed with water and dried in an air flow. A greenish, strongly iridescent layer comprising zinc/chromium oxide formed on the pieces. The sample was subjected to a corrosion test in a salt spray cabinet according to DIN 50021 SS. It was surprisingly found that the chromate layer formed presented excellent corrosion protection until the appearance of first corrosion products of 1000 hrs. according to DIN 50961, Chapter 10, in particular Chapter 10.2.1.2.

The novel greenish chromate layer had a layer thickness of approx. 800 nm and was produced by a process not involving any chromium(VI) and could be proven to be chromium(VI)-free. The production method for the novel, greenish chromium(VI)-free chromation described above is not very economical for use in conventional plants, due to the relatively high temperature required by the process solution. Further theoretical considerations concerning chromium(VI)-free chromate coatings, and further trials, finally resulted in far more economical production conditions.

### **Example 2: Coating of Zinc Coated Steel Pieces**

Electrolytically bright-zinc coated (15  $\mu\text{m}$ ) steel parts were immersed for 60 sec. in an aqueous chromate coating solution

containing

50 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt),  
100 g/l  $\text{NaNO}_3$ , and  
31,2 g/l malonic acid.

the pH of which having been previously adjusted to 2.0 with sodium hydroxide solution. The samples were then rinsed and dried, and subjected to a corrosion test in a salt spray cabinet according to DIN 50021 SS. The sample exhibited a corrosion protection of 250 hrs. until first attack according to DIN 50961.

Malonic acid is a ligand enabling more rapid ligand replacement kinetics at the chromium(III) than the fluoride of Example 1. Good corrosion protection, by far exceeding the minimum requirement of DIN 50961 for Method Group C (yellow chromation), may thus already be achieved at 60°C.

**Example 3: Coating of Zinc Coated Steel Pieces**

Electrolytically bright-zinc coated (15  $\mu\text{m}$ ) steel parts were immersed for 60 sec. in an aqueous chromate coating solution consisting of

50 g/l  $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$  (trivalent chromium salt),  
3 g/l  $\text{Co}(\text{NO}_3)_2$ ,  
100 g/l  $\text{NaNO}_3$ , and  
31.2 g/l malonic acid,

previously adjusted to pH 2.0 with a sodium hydroxide solution. The samples were then rinsed and dried, and subjected to the same corrosion test in the salt spray cabinet according to DIN 50021 SS. The samples exhibited a corrosion protection of 350 hrs. until first attack according to DIN 50961.

Cobalt is an element which is capable, in accordance with the invention, of catalyzing ligand replacement and reducing reverse reaction II by insertion of kinetically stable oxides into the chromate layer. The thus produced chromate layer is thus thicker. The concept advanced by the present inventors has, thus, been experimentally verified. Corrosion enhanced protection was compared with Example 3 by the sole addition of Cobalt into the

chromate coating solution.

Novel greenish chromate layers were also produced on zinc surfaces as described in Example 2, except that the temperature was 40, 60, 80 and 100°C. The thicknesses of the respective chromate layers were determined by RBS (=Rutherford-Backscattering) testing. The corresponding corrosion protection values in hours of salt spray cabinet exposure according to DIN 50021 SS until first attack according to DIN 50961 Chapter 10 are listed in Table 4 below.

Table 4: Corrosion Protection Values

J/°C	Thickness / nm	Corr. Prot. / hrs.
40	100	50-60
60	260	220-270
80	400	350 450
100	800	800-1200

Depending on the complex ligands used, e.g. malonate in Examples 2 and 3, it is possible to achieve even considerably higher layer thicknesses and corrosion protection values. Complex ligands containing nitrogen, phosphorus or sulfur as the complexing functional group, e.g.  $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical, and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H, are also used in embodiments of this invention. With these ligands, it is possible to produce the excellent indicated layer properties (within limits) even at room temperatures.

Example 4: Zn/Fe Alloy Coated Steel Pieces

Steel pieces electrolytically coated with a zinc/iron alloy (0.4-0.6% iron) were immersed for 60 sec. at 60°C in the following aqueous chromate coating solution: